Sulphur-tolerant Homogeneous Catalysts for the Water Gas Shift Reaction

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Summary The transition metal carbonyls $M(CO)_6$ (M = Cr, Mo, and W) and $M_3(CO)_{12}$ (M = Ru and Os), but not $Fe(CO)_5$, have been found to be active homogeneous catalysts for the water gas shift reaction in the presence of a large excess of sulphides generated by sodium sulphide dissolved in aqueous methanol.

TRANSITION metal carbonyl compounds which function as homogeneous catalysts for the water gas shift (w.g.s.) reaction have been the subject of considerable research in the last few years,[1—6] mainly because these systems operate under considerably milder conditions than conventional heterogeneous catalysts.† Furthermore, as can be seen from equation (1), both the reactant CO, from synthesis gas, and the products are gases, thus eliminating the problem of catalyst separation from reactant and product streams.

$$CO(g) + H_2O(l) \rightleftharpoons H_2(g) + CO_2(g) \qquad (1)$$

$$\Delta G^0_{298} \; -4{\cdot}76 \text{ kcal mol}^{-1} \; (19{\cdot}9 \text{ kJ mol}^{-1})$$

Since sulphur-containing impurities are expected to be present in many synthesis gas feedstocks for a water gas shift reactor, any practical catalyst system must exhibit a high degree of tolerance towards sulphur. This communication reports experiments which show that a number of homogeneous w.g.s. catalyst systems are quite tolerant towards sulphur, and are therefore promising candidates for commercial use.

The catalysts (or catalyst precursors) are the mononuclear carbonyls of group 6B metals, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ and the group 8B metal carbonyls, $Fe(CO)_5$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$. With the exception of $Os_3(CO)_{12}$, each of the above species has been shown to be catalytically active towards the w.g.s. reaction.[2,4]

The w.g.s. reactions were all carried out in small (700 ml), unlined stainless steel autoclaves mounted in shielded ovens. Temperatures were maintained at 160 ± 1 °C using proportional controllers and the liquid phase was stirred magnetically. The rates of formation and consumption of the respective gaseous species in equation (1) were monitored, with respect to time, by gas chromatography using a Fisher Model 1200 gas partitioner having a 6½ ft 80—100 mesh Columnpak PQ column followed by an 11 ft 13X molecular sieve column. A Varian CDS-III digital integrator was used to integrate the output from the gas partitioner. Argon was used as an internal standard, and helium as the carrier gas. Care was taken to ensure that all hydrogen analyses were performed at column loadings within the linear response region of the sensitivity curve. A more complete description of the experimental equipment and techniques is in ref. 6.

Each of the catalyst systems studied here operate under basic conditions. Therefore in order to examine the performance of these catalysts in the presence of high concentrations of sulphur, a simple test was devised; namely sodium sulphide (58 mmol) was substituted for potassium hydroxide (39 mmol) as the base component in the initial reaction mixture, which consisted of a small amount of catalyst [0·126 mmol of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$, 2·23 mmol of $Fe(CO)_5$, and 0·021 mmol of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$] dissolved in 200 ml of a 25% (v/v) solution of water in methanol. The temperature of 160 °C proved convenient for comparing reaction rates in the presence of these two bases. At this relatively low temperature the w.g.s. reaction proceeds slowly towards completion thus allowing ample time for any deleterious side reactions to occur. It is difficult to imagine a more severe test of sulphur tolerance for these catalyst systems, since the hydrolysis of sodium sulphide provides both HS^- and H_2S during the course of the w.g.s. reaction, equations (2) and (3).‡

$$S^{2-} + H_2O \rightleftharpoons HS^- + OH^- \qquad (2)$$

$$HS^- + H_2O \rightleftharpoons H_2S + OH^- \qquad (3)$$

Typical data are shown in the Figure where the rates of hydrogen production by the w.g.s. reaction catalysed by $W(CO)_6$ in the presence of KOH and Na_2S are compared. The substitution of sodium sulphide for potassium hydroxide has only a slight inhibitory effect upon the catalytic activity of $W(CO)_6$.

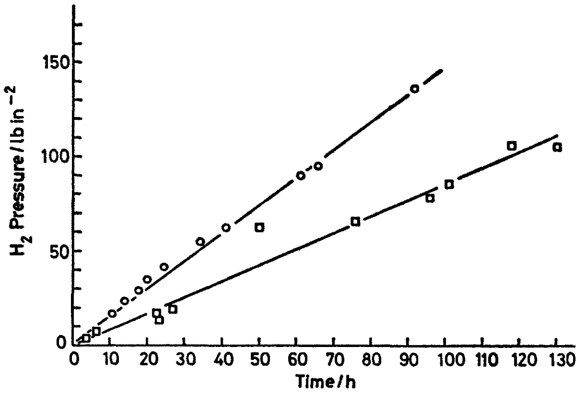

FIGURE. Production of hydrogen as a function of time using $W(CO)_6$. ○: KOH; □: Na_2S.

The Table contains the results of identical experiments carried out with the other transition metal carbonyls. These data indicate that, with the exception of $Fe(CO)_5$, the

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† Heterogeneous catalysis of the w.g.s. reaction using current technology requires temperatures above 300 °C, whereas a number of homogeneous catalyst systems cited in Refs 1—6 exhibit highly catalytic activities at temperatures ranging from 100 to 200 °C.

‡ The sulphur content of the system containing Na_2S corresponds to a sulphur impurity level of 11,000 p.p.m. Because of the strong basicity of the sulphide ion, the sulphur will be predominantly in the form of HS^- ($[HS^-]$ *ca.* 0·023 M). At later stages of the reaction when the pH has fallen to a typical value of 8, appreciable amounts of the sulphur are present in the form of hydrogen sulphide ($[H_2S]$ *ca.* 0·04 M).

TABLE. Comparison of hydrogen production rates from the water gas shift reaction catalysed by various transition metal carbonyls using potassium hydroxide and sodium sulphide as bases.[a]

Metal carbonyl	Rate with KOH[b]	Rate with Na_2S[b]	Rate with Na_2S/ Rate with KOH (%)
$Cr(CO)_6$	280	60	21
$Mo(CO)_6$	220	130	59
$W(CO)_6$	270	180	67
$Fe(CO)_5$	650	0	0
$Ru_3(CO)_{12}$	870	550	63
$OS_3(CO)_{12}$	210	200	95

[a] Each experiment was identical with respect to loading pressure of carbon monoxide ($P_{CO} = 400$ lb in^{-2} at 25 °C), and solvent (200 ml H_2O-MeOH, 25:75 v/v) containing 39 mmol KOH or 58 mmol Na_2S, respectively. The experiment with $Fe(CO)_5$ was conducted at 140 °C, and all others at 160 °C. Amounts of catalyst used are listed in the text. [b] The rates are expressed as turnover numbers per day, as calculated over the first 90 h of each experiment (mol H_2/day)/(mol metal carbonyl).

other catalyst systems are also tolerant towards sulphur to varying degrees. Among the carbonyl derivatives of each periodic group (Cr, Mo, W, and Fe, Ru, Os) inhibition by sulphur diminishes with increasing atomic number of the central metal atom(s), as shown in the third column of the Table.

In the case of $Fe(CO)_5$, no catalytic activity was observed in the presence of Na_2S. The alcoholic solution remaining after 90 h at 140 °C under the conditions listed in the Table was dark red. Extraction with dichloromethane and evaporation of the extract *in vacuo* led to dark red crystals which were dissolved in pentane. Filtration and evaporation gave red crystals of the known[7] $Fe_3(CO)_9S_2$,§ identified by its i.r. spectrum. This suggests that a rapid reaction of $Fe(CO)_5$ with sodium sulphide, to produce $Fe_3(CO)_9S_2$, is responsible for the poisoning of this catalyst system at high sulphide concentrations.

The data reported here indicate that a number of simple carbonyl derivatives of group 6B and 8B metals, particularly those of the heavier metals, offer great promise in catalyst systems for enriching the hydrogen content of synthesis gas even in the presence of sulphur-containing impurities.

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§ The physical properties of $Fe_3(CO)$ S_2 are reported in R. B. King, *Inorg. Chem.*, 1963, **2**, 326.

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